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# SAMPLING AND ANALYSIS OF SELECTED TOXIC SUBSTANCES

## TASK III: VINYL CHLORIDE, SECONDARY SOURCES

MIDWEST RESEARCH INSTITUTE

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## Task III - Vinyl Chloride, Secondary Sources

Environmental Protection Agency
Office of Toxic Substances
Washington, D.C. 20460

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16. ABSTRACT

A sampling and analysis program was conducted to determine whether and to what extent vinyl chloride was present in ambient air due to the presence of polyvinyl chloride products. Sampling environments were chosen to represent real life, but nonwork situations where a significant exposure to polyvinyl chloride products might occur. A sampling and analysis protocol was developed with a recovery efficiency of greater than 90% and a detection limit of 10 ppb (v/v).

The two general categories of environments sampled were vehicles and commercial products. The interior ambient air was sampled from new and used domestic automobiles, foreign automobiles and domestic mobile homes. No evidence of vinyl chloride was found. The following commercial vinyl products, when sampled in their normal environment, did not produce a measurable quantity of vinyl chloride in the ambient air: vinyl wall covering; vinyl swimming pool liners; and vinyl nursery products. A room being painted with a heavily pigmented red paint was found to contain a very low level of vinyl chloride.

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## Task III - Vinyl Chloride, Secondary Sources

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## SECTION I

## SUMMARY AND CONCLUSIONS

A sampling and analysis program was conducted to determine whether and to what extent vinyl chloride was present in ambient air due to the presence of polyvinyl chloride products. Sampling environments were chosen to represent real life, but nonwork situations where a significant exposure to polyvinyl chloride products might occur.

The air samples were collected by drawing a known volume of air through a tube of activated charcoal. The trapped vinyl chloride was desorbed by carbon disulfide at dry ice temperature. The overall trapping and desorption efficiency was generally greater than 90%. The carbon disulfide extracts were analyzed for vinyl chloride by gas chromatography using flame ionization detection. Two different columns were routinely employed to confirm identity. With the sampling and analysis protocol normally employed, the detection limit was 10 ppb (v/v).

The two general categories of environments sampled were vehicles and commercial products. The interior ambient air of the following vehicles were sampled: Chevrolets--1976, 1975; Ford--1976, 1975, 1974; Plymouth--1976, 1975, 1974; AMC--1976, 1975, 1974; Volkswagen--1976, 1975, 1974; Toyota--1976, 1975; Skyline mobile home-new and used; and Champion mobile home--new and used. No evidence of vinyl chloride was found. The following commercial vinyl products, when sampled in their normal environment, did not produce a measurable quantity of vinyl chloride in the ambient air: vinyl wall covering; vinyl swimming pool liners; and vinyl nursery products--mattress pad, bumper pads, changing table pad, playpen pad, and toy box. Samples of vinyl shower curtains and pull shades, confined in a small sealed chamber, did not release measurable levels of vinyl chloride. A 12 x 10 x 12 ft room painted with ca 3-1/2 gal. of Tomato Red paint, obtained from Cook Paint Company, was found to contain a small but measurable level of vinyl chloride. The levels were in ppb (v/v): 22 during painting, 4 during and after painting, and not detectable 1 day later.

## SECTION II

## INTRODUCTION

The objective of this program is to provide the Environmental Protection Agency with sampling and analysis capabilities to determine the levels of toxic substances in air, water, soil, and other miscellaneous samples from designated sources and ambient locations throughout the United States. The toxic substance studied in this task was vinyl chloride.

The origin of this task was the Vinyl Chloride Task Force Recommendation No. 4--"A program should be initiated to determine whether and to what extent background levels of vinyl chloride are present in the ambient air--indoors and outdoors--due to the presence of polyvinyl chloride products." This report contains a discussion of the selection of sampling environments, the development of a sampling and analysis protocol, and the presentation and discussion of the results for vehicles and commercial products.

## SECTION III

## SCREENING AND SELECTION OF SAMPLING ENVIRONMENTS

The task called for the selection of sites or environments at which an exposure to vinyl chloride existed due to the presence of polyvinyl chloride products. The following environments were specified:

A. Vehicles

1. Domestic automobiles;
2. Foreign automobiles;
3. Mobile homes; and
4. Recreational vehicles.

B. Commercial products

1. Latex paint;
2. Vinyl wall covering;
3. Vinyl fabric; and
4. Nursery equipment.

In all cases, duplicate samples were to be collected for analysis.

The principle criteria in site selection was that the environment be in a real life but nonwork place situation. In all instances, cooperation of the appropriate dealer or user of a product was obtained prior to sampling. Additional criteria were imposed with the selection of specific environments.

## VEHICLES

Whenever possible, sampling was conducted on a relatively warm day between 10:00 a.m. and 4:00 p.m. Vehicles were chosen, if available, that had dark exterior and interior finishes. In all instances, the vehicles were on the sales lot and were not running.

### Domestic Automobiles

A 1976 compact or family sized passenger vehicle was selected from the Ford, Chevrolet, Plymouth, and AMC lines. Comparable 1975 and 1974 models were also sampled when they were available.

### Foreign Automobiles

One 1976 top selling passenger vehicle was chosen from the Datsun, Toyota, and Volkswagen lines. Comparable 1975 and 1974 models were also sampled when available.

### Mobile Homes

One new and one used mobile home each were chosen from the Skyline and the Champion lines. The vehicles sampled all had white exteriors.

### Recreational Vehicles

Models were chosen from the best-selling lines of self contained motor homes, trailer-type campers, and slide-in campers. All vehicles were produced by Fleetwood Enterprises, Inc.

## COMMERCIAL PRODUCTS

Generally sampling was conducted during real-life situations. Occasionally, products were analyzed in the laboratory under severe conditions to determine if any potential existed for vinyl chloride emission.

### Latex Paint

The base of latex paint is an organic homo- or heteropolymer. Common polymers used for interior or exterior paints have been polyvinyl acetate, polyacrylates, or copolymers of vinyl acetate and acrylate. Five paint companies surveyed in the preparation of this report, Benjamin Moore, Pratt and Lambert, Colony Paint, Great Western, and Davis, stated that no polyvinyl chloride is used in the formulation of their paints. Cook Paint Company reported that a terpolymer of vinyl chloride, vinyl acetate, and ethylene is used in a minor portion of their line. The terpolymer, obtained as Airflex 728 from Air Products and Chemicals, is used in

the formulation of what is termed Accent paints. These are paints which are highly pigmented, with deep or dark colors. Since the probability of finding a real-life use of these specific paints was quite low, a room at MRI was selected for painting with this paint.

Vinyl Wall Covering

A retail wall covering outlet having an appreciable display stock was desired for sampling. The site that was chosen, Dwoskins, maintained a large display stock and a significant warehouse stock, and both areas were sampled. An environment in which vinyl wall coverings were being installed was also desired. For reasons discussed later, this environment was not sampled.

Vinyl Fabric

An environment was desired in which commercial vinyl fabrics such as shower curtains or vinyl window shades were to be installed. For reasons discussed later, these products were analyzed in the laboratory and no real-life situations were tested. Also, a retail outlet carrying an appreciable stock of vinyl products was sampled. The outlet chosen sold vinyl swimming pool liners.

Nursery Equipment

An environment was desired in which new nursery equipment was to be installed. The newly equipped nursery of an expectant MRI employee was chosen for sampling.

## SECTION IV

## DISCUSSION OF SAMPLING ENVIRONMENTS

Details of each sampling environment are described below. When appropriate, diagrams showing the location of potential sources, samplers, etc., are presented.

### VEHICLES

#### Domestic Automobiles

The domestic automobiles were sampled at the following locations: AMC, Friendly AMC, 7712 Wornall, Kansas City, Missouri; Chevrolet, Pappas Chevrolet, 115 West Gregory, Kansas City, Missouri; Ford, Southtown Ford, 1326 East 47th, Kansas City, Missouri; Plymouth, Downtown Plymouth, 8625 Troost, Kansas City, Missouri. The sampling equipment was placed inside the vehicle with an on/off switch for the pump placed outside the vehicle. The charcoal adsorption tubes were situated at head height midway between the driver and the front seat passenger. After installation of the sampling equipment, a period of 30 min was allowed to pass before collecting air samples. Table 1 summarizes the relevant data collected at the time of sampling.

#### Foreign Automobiles

The foreign automobiles were sampled at the following locations: Toyota, Toyota of Kansas City, Inc., 1325 Bannister Road, Kansas City, Missouri; and Volkswagen, Bunker Volkswagen, Inc., 7800 Wornall, Kansas City, Missouri. The location and operation of the sampling equipment was identical to that of the Domestic Automobiles. Relevant data pertaining to the sampling is summarized in Table 1.

#### Mobile Homes

The mobile homes were sampled at the following locations: Champion, K and H Mobile Homes, St. Joseph, Missouri; and Skyline, Pitts Mobile Homes, 8747 East 40 Highway. Sampling stations were located in the bedroom, the living room, and the kitchen at a height of 4 ft. The units

Table 1. SAMPLING DATA

| Environment or site location | Date | Times | Temperature | Volume sampled (ℓ) |
|---|---|---|---|---|
| **Vehicles** | | | | |
| Domestic automobiles | | | | |
| Chevrolet | | | | |
| 1976 Malibu station wagon, red with with brown interior | 10/10/75 | 1315-1345 | Air - 31°C<br>Seat - 29°C | 2.65, 3.23 |
| 1975 Impala, brown with brown interior | 10/10/75 | 1505-1535 | Air - 35°C<br>Seat - 32°C | 3.29, 3.35 |
| Ford | | | | |
| 1976 Gran Torino, blue with blue interior | 10/11/75 | 1325-1355 | Air - 39°C<br>Seat - 42°C | 3.15, 3.44 |
| 1975 Gran Torino, brown with brown interior | 10/11/75 | 1205-1235 | Air - 43°C<br>Seat - 45°C | 3.60, 3.90 |
| 1974 Gran Torino, brown with brown interior | 10/11/75 | 1445-1515 | Air - 32°C<br>Seat - 29°C | 3.08, 3.09 |
| Plymouth-Chrysler | | | | |
| 1976 Valiant, black with black interior | 10/13/75 | 1200-1230 | Air - 24°C<br>Seat - 20°C | 3.48, 3.66 |
| 1975 Duster, tan with tan interior | 10/13/75 | 1330-1400 | Air - 26°C<br>Seat - 23°C | 2.27, 4.50 |
| 1974 Duster, metallic brown with brown interior | 10/13/75 | 1445-1515 | Air - 25°C<br>Seat - 25°C | 3.23, 3.68 |
| AMC | | | | |
| 1976 Hornet, tan with brown interior | 11/17/75 | 1245-1315 | Air - 33°C<br>Seat - 32°C | 2.25, 4.29 |
| 1975 Hornet, tan with brown interior | 11/17/75 | 1435-1505 | Air - 30°C<br>Seat - 34°C | 3.05, 3.63 |
| 1974 Matador, black with black interior | 11/17/75 | 1400-1430 | Air - 29°C<br>Seat - 27°C | 2.63, 3.30 |
| Foreign automobiles | | | | |
| Volkswagen | | | | |
| 1976 Rabbit, green with tan interior | 11/18/75 | 1430-1500 | Air - 27°C<br>Seat - 26°C | 1.55, 3.00 |
| 1975 Rabbit, green with black interior | 11/18/75 | 1315-1345 | Air - 29°C<br>Seat - 26°C | 2.66, 3.15 |
| 1974 Beetle, gold with brown interior | 11/18/75 | 1130-1200 | Air - 28°C<br>Seat - 25°C | 3.11, 3.34 |
| Toyota | | | | |
| 1976 Corolla, red with black interior | 11/19/75 | 1120-1150 | Air - 21°C<br>Seat - 20°C | 2.25, 3.19 |
| 1975 Corona, gray with black interior | 11/19/75 | 1310-1340 | Air - 24°C<br>Seat - 24°C | 3.19, 3.20 |
| Mobile homes | | | | |
| Skyline | | | | |
| New, 70 x 14 ft, two bedroom, white | 11/6/75 | | | |
| Far bedroom | | 1045-1115 | Air - 20°C | 0.58, 3.03 |
| Living room | | 1130-1200 | Air - 20°C | 2.43, 2.68 |
| Kitchen | | 1220-1250 | Air - 20°C | 2.01, 3.70 |
| Used (1970), 70 x 14 ft, two bedroom, white | 11/6/75 | | | |
| Far bedroom | | 1450-1525 | Air - 22°C | 2.92, 4.20 |
| Living room | | 1535-1605 | Air - 22°C | 2.73, 4.69 |
| Kitchen | | 1610-1640 | Air - 22°C | 3.35, 4.02 |

Table 1. (concluded)

| Environment or site location | Date | Times | Temperature | Volume sampled (ℓ) |
|---|---|---|---|---|
| Champion | | | | |
| New, 70 x 14 ft, two bedroom, white | 11/11/75 | | | |
| Far bedroom | | 1100-1130 | Air - 7°C | 2.60, 4.86 |
| Living room | | 1135-1205 | Air - 7°C | 3.15, 3.27 |
| Kitchen | | 1210-1240 | Air - 7°C | 2.81, 4.56 |
| Used, 60 x 12 ft, two bedroom, white | 11/11/75 | | | |
| Far bedroom | | 1315-1345 | Air - 8°C | 2.95, 5.18 |
| Living room | | 1400-1430 | Air - 8°C | 3.14, 5.81 |
| Kitchen | | 1440-1510 | Air - 8°C | 2.82, 7.56 |
| Commercial products | | | | |
| Latex paint | | | | |
| Test room, 12 x 10 x 12 ft, painted | 12/9/75 | 1130-1200 | Air - 23°C | 0.73, 2.69 |
| 0900-1200, 1300-1500 on 12/9/75 | 12/9/75 | 1300-1700 | | 17.55 |
| | 12/10/75 | 0900-1300 | Air - 22°C | 39.60 |
| Vinyl wall covering | | | | |
| Warehouse | 11/25/75 | 1005-1035 | Air - 18°C | 1.34, 2.21 |
| Showroom | 11/25/75 | 1110-1140 | Air - 23°C | 2.28, 3.00 |
| Vinyl fabrics | 11/25/75 | | Air - 19°C | |
| Swimming pool lines, single large pool | | 1415-1445 | | 1.64, 3.57 |
| Swimming pool lines, two small pools | | 1510-1540 | | 1.79, 4.27 |
| Nursery equipment | | | | |
| Crib corner | 12/2/75 | 0900-0930 | Air - 28°C | 1.37, 2.16 |
| Crib center | 12/2/75 | 0940-1010 | Air - 28°C | 1.49, 3.66 |
| Changing table | 12/2/75 | 1030-1100 | Air - 28°C | 1.70, 4.33 |
| Toy box | 12/2/75 | 1115-1145 | Air - 28°C | 3.88, 4.68 |
| Crib corner | 12/3/75 | 1020-1050 | Air - 27°C | 1.62, 2.58 |
| Crib center | 12/3/75 | 1055-1125 | Air - 27°C | 1.54, 2.54 |
| Changing table | 12/3/75 | 1145-1215 | Air - 27°C | 2.11, 2.63 |
| Toy box | 12/3/75 | 1230-1300 | Air - 27°C | 1.68, 3.73 |
| Playpen pad | 12/22/75 | 2000-2200 | Air - 26°C | 10.12, 10.49 |

were closed for at least 30 min before air samples were collected. Table 1 summarizes the relevant data collected at the time of sampling.

Recreational Vehicles

No samples were collected from recreational vehicles for several reasons. No vinyl chloride had been detected in any of the automobiles or mobile homes that had been sampled. Furthermore, the ambient temperature had dropped to ca 0°C which would decrease the possibility of vinyl chloride emission.

COMMERCIAL PRODUCTS

Latex Paint

An unoccupied room at MRI, removed from the laboratory areas, was used for testing latex paint. The room was 12 x 10 x 12 ft with normal ventilation. During painting and sampling, the door was kept closed. The sampler was positioned 1 m from the wall at a height of 1 m. Two coats of paint were applied between 0900 and 1500; however, no painting was done between 1200 and 1300. Approximately 3-1/2 gal. of paint was applied. The paint was Tomato Red, Code 002, obtained from the Cook Paint Company, Kansas City, Missouri. As a precaution, the painter was required to wear a carbon filter mask while painting. Sampling data are summarized in Table 1.

Vinyl Wall Covering

Air samples were collected from the showroom and the warehouse at Dwoskin, 10770 El Monte, Kansas City, Kansas. One sample station was positioned in the showroom next to a display of vinyl wall coverings. The second sampler was positioned in the center of the 20 x 40 m warehouse containing a large supply of rolled wall coverings. A strong odor was present at both locations. Sampling data are summarized in Table 1.

A sample of vinyl wallpaper paste was tested for vinyl chloride by placing 6 g in a 7.5 ml vial fitted with a septum. After 1 hr at ambient temperature, head space air samples were removed for analysis using gas tight syringes. The vial was heated to 60°C for 1 hr and the test repeated.

Vinyl Fabrics

An air sample from a vinyl fabric environment was collected at the Esther Williams Pool Company, 6231 Troost, Kansas City, Missouri. Three swimming pool liners were on display in a showroom. The pools were circular with diameters of approximately 10.5 and 5 m and depths of 1 m. Air

samples were collected immediately adjacent to the pools. Sampling data are summarized in Table 1.

Other vinyl fabrics sampled were a vinyl shower curtain and a vinyl pull shade. Both were purchased from a local T.G.&Y. store. The shower curtain was gold print and carried the name Drapecraft. The white pull shade was manufactured by Clopay Corporation, Cincinnati, Ohio.

In both cases, initial screening experiments were performed by placing the product in a closed chamber and sampling the head space. A portion of the vinyl window shade 86 x 90 cm, weighing 117 g (approximately 30% of the curtain), was placed in a 1.0 liter screw-top jar fitted with a septum. Air samples were collected by gas tight syringe periodically for up to 2 hr at ambient temperature. The jar was also heated to 60° C for 1/2 hr and air samples collected with a gas-tight syringe.

A 37 x 177 cm portion of vinyl shower curtain, weighing 92.8 g (approximately 20% of the shade), was placed in a 1.0 liter jar equipped with a septum. With the jar at ambient temperature, air samples were removed with an air-tight syringe and analyzed periodically for 2 hr. The jar was then heated to 60° C for 1/2 hr and air samples analyzed as before.

Nursery Equipment

The nursery equipment was located in a 10 x 11 ft room arranged as shown in Figure 1. The following new items were installed in the room immediately before sampling was begun.

1. Vinyl mattress cover;
2. Vinyl covered bumper pads;
3. Vinyl covered wastebasket;
4. Vinyl covered toy chest;
5. Assortment of plastic toys;
6. Vinyl covered changing table pad; and
7. Vinyl diaper bag.

Samples were collected at the center and at a corner of the crib, at the surface of the changing table, and adjacent to the toy chest, toys and vinyl wastebasket. A new playpen pad was installed in a playpen, and air samples were collected at its center. Sampling data are summarized in Table 1.

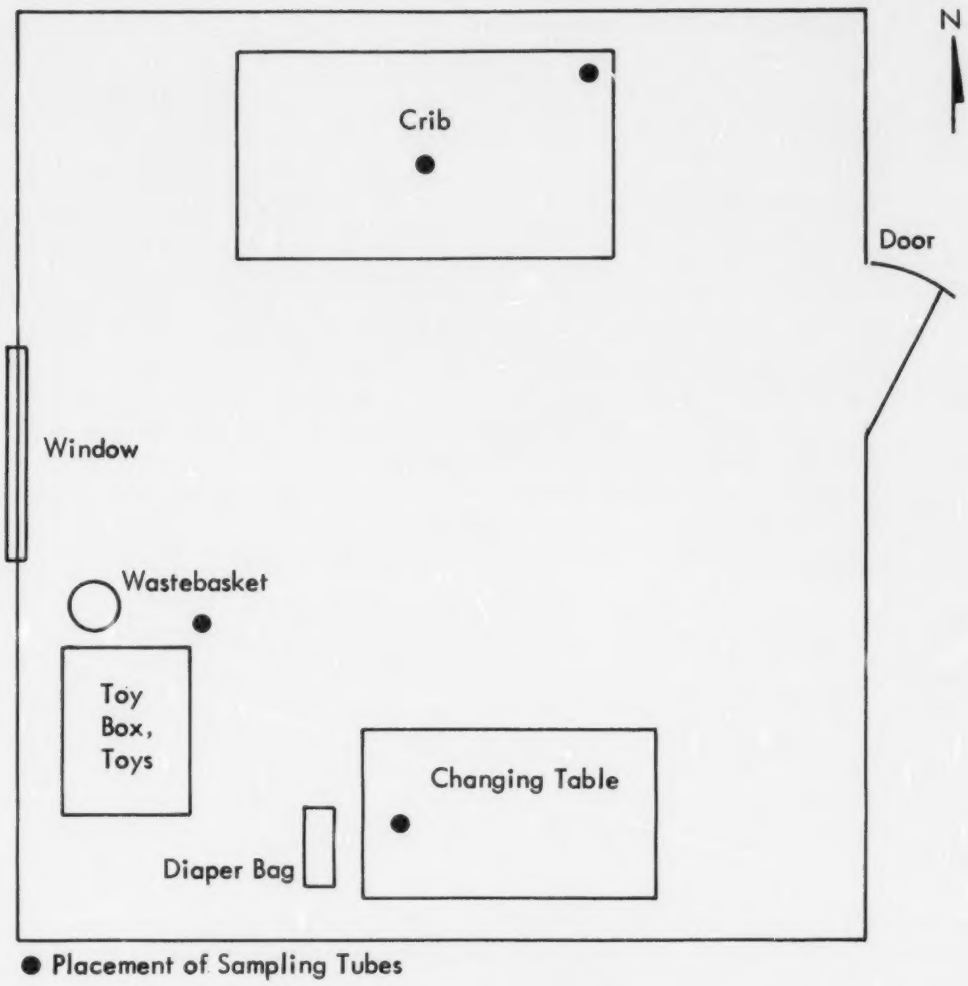



Figure 1. Location of nursery equipment

## SECTION V

## DEVELOPMENT OF SAMPLING AND ANALYSIS PROTOCOL

### METHOD DEVELOPMENT AND EVALUATION

The generally accepted procedure for determining vinyl chloride in air utilizes the trapping of vinyl chloride on activated charcoal followed by its desorption from charcoal using carbon disulfide. A well-defined protocol is necessary to maintain acceptable recovery and precision. It is customary and highly advisable that each laboratory conducting vinyl chloride analyses thoroughly evaluate their protocol and establish overall recovery values. The critical steps which were evaluated separately in this study were: (a) preparation of charcoal adsorption tubes; (b) efficiency of collection; (c) stability of the collected samples; and (d) desorption efficiency of carbon disulfide.

### PREPARATION OF CHARCOAL ADSORPTION TUBES

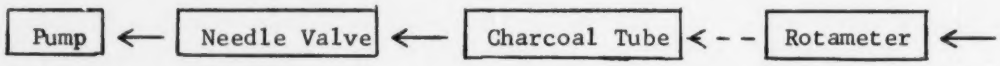
As charcoal is a well-known adsorbent of organic vapor, it was necessary to be able to prepare a charcoal which was free of any organic material which could interfere with the analysis.

Coconut charcoal, 6 to 14 mesh, obtained from Fisher Chemical, was heated to 250° C for 2 hr in a stream of purified nitrogen. After cooling, the charcoal was transferred to a glass jar and bathed with nitrogen before capping. Stainless steel tubes, 3 x 1/4 in., were packed with about 400 mg charcoal and plugged with glass wool at both ends. Care was taken to leave space at one end which was then marked Inlet. The ends were covered with precleaned aluminum foil and plastic caps, and the tubes were stored in a closed jar under nitrogen. Prior to use, the individual tubes were heated in an oven at 275° C for 15 min under nitrogen. Tubes prepared in this fashion showed no peaks near the retention volume of vinyl chloride at maximum sensitivity.

## SAMPLE COLLECTION AND STORAGE

### Sampling

Experiments were performed to determine the collection efficiency and the breakthrough point of the charcoal tubes for vinyl chloride. A stream of 10 ppm vinyl chloride in nitrogen was sampled continuously through two charcoal traps in series. The stream was sampled at 100 ml/min. The vinyl chloride was generated by calibrated permeation tubes. After 255 min, the traps were removed and immediately analyzed for vinyl chloride. More than 99.7% of the total vinyl chloride trapped was found on the first tube. The adopted sampling protocol was designated as 30 to 120 min with the capability of extension to 240 min if desired. Air samples were collected using the train shown below.




Air was pulled through the tube at 100 ml/min for a given time. Flow rates were controlled by a needle valve and checked at the beginning, the midpoint, and at the end of the sampling period.

### Storage

Once the charcoal tubes are used to collect vinyl chloride, it is necessary to know if they are stable and how long they can be stored prior to analysis.

A series of charcoal tubes were loaded by sampling 4 ppm nitrogen at 100 ml/min for 10 min. The tubes were capped and stored in crushed dry ice until analyzed. The tubes were analyzed periodically for up to 7 days after collection. Recoveries were high as expected within the first 24 hr. Tubes stored longer than that began to show low recoveries. Since all the tubes were prepared at the same time in an identical fashion, the drop in recovery must be related to storage time.

An experiment was devised to test for loss of vinyl chloride by volatilization. It was felt that the most serious loss would occur at the inlet end of the tube since that is where the majority of the adsorbed vinyl chloride is trapped. Vinyl chloride migrating down the tube, toward the outlet would be readsorbed by the charcoal. Vinyl chloride diffusing toward the inlet end, however, would not be readsorbed and could be lost. Tubes were loaded with vinyl chloride by collecting a gas sample from the permeation tube. Approximately 50 mg of charcoal was immediately added to the inlet end of the tube and the tube was plugged with glass wool. After recapping, the tubes were stored in dry ice until analyzed.

The results are summarized in Table 2. Tubes analyzed with 24 hr after collection generally gave acceptable recoveries without supplementary charcoal. Beyond 1 day, recoveries were low and variable. The tubes prepared with supplementary charcoal gave high recoveries for up to 5 days after collection. As expected, a significant fraction of the vinyl chloride was present on the added charcoal.

## REMOVAL OF VINYL CHLORIDE FROM CHARCOAL WITH CARBON DISULFIDE

The trapped vinyl chloride is readily extracted from charcoal with carbon disulfide. The reaction of charcoal and carbon disulfide, however, is highly exothermic and localized boiling can occur. Due to the high volatility of vinyl chloride, care is necessary in this step to avoid its loss. It is necessary to establish both the time required for complete desorption and the efficiency of desorption.

Vials with a 3.5 ml capacity were fitted with Rubber-Teflon® laminated discs (Teflon® side down) and open top screw caps. The vials were set in crushed dry ice and 2 ml carbon disulfide were added. All of the charcoal from the adsorption tubes was slowly added to the cooled vial. The glass wool plugs were discarded. The cap was replaced and the vial was left in the dry ice. At various intervals, a 5 µl sample was withdrawn and analyzed. Recovery was constant from 25 to 140 min after mixing. In the adopted protocol, a 30 min waiting time was used.

The total recovery for nine tubes loaded with 11 to 13 µg vinyl chloride, and analyzed by the recommended protocol, averaged 96.6% with an estimated standard deviation of 7.3%. A measure of percent recovery at very low loadings was also made, and the results are reported in Table 3.

## GAS CHROMATOGRAPHIC ANALYSIS

Vinyl chloride was analyzed by gas chromatography using hydrogen flame ionization detection. Two columns were used for separation and confirmation of identity. The first column (Column 1) was 6 ft x 1/8 in. stainless steel, packed with 80/100 mesh Chromosorb 102, followed by 6 ft x 1/8 in. stainless steel, packed with 10% DC-200 on 100/120 Supelcoport. The second column (Column 2) was 6 ft x 1/8 in. stainless steel, packed with 0.4% Carbowax 1500 on Carbopak A. Operating conditions and temperatures are summarized in Table 4.

Calibration curves were prepared by injecting 0.050 to 1.00 ml samples of vinyl chloride in nitrogen. The gas samples were obtained from a calibrated permeation tube apparatus that was adjusted to provide a stream of nitrogen containing from 0.6 to 100 ppm (v/v) vinyl chloride. Calibration curves ranged from 0.25 to 9.85 ng/injection and were linear. A reasonable limit of detection was 0.1 ng.

Table 2. EFFECT OF STORAGE TIME ON RECOVERY OF VINYL CHLORIDE

I. Percent recovery - no additional charcoal

| Run No. | Time before analysis | % Recovery |
|---|---|---|
| 1 | 1 to 4 hr | 93, 103, 80, 90, 86, 90 |
| 2 | 24 hr | 97, 93, 54 |
| 3 | 2 to 7 days | 53, 44, 71, 87, 63 |

II. Percent recovery - charcoal added to inlet

| Run No. | Time before analysis | % Inlet | % Main | Total % recovery |
|---|---|---|---|---|
| 4 | 2 to 4 hr | 1.4 | 87.8 | 89.2 |
| 5 | 2 to 4 hr | 2.3 | 97.7 | 100.0 |
| 6 | 2 to 4 hr | 4.1 | 90.1 | 94.2 |
| 7 | 24 hr | 10.5 | 97.5 | 108.0 |
| 8 | 24 hr | 14.6 | 76.2 | 90.8 |
| 9 | 24 hr | 10.4 | 97.0 | 107.4 |
| 10 | 5 days | 9.9 | 81.7 | 91.6 |
| 11 | 5 days | 15.4 | 83.3 | 98.7 |
| 12 | 5 days | 9.2 | 80.5 | 89.7 |

Table 3. RECOVERY OF VINYL CHLORIDE AT DIFFERENT LOADINGS

| Nanograms sampled | Nanograms found | % Recovery |
|---|---|---|
| 11,000-13,000 | | 96.6 |
| 768 | 603 | 79 |
| 384 | 247 | 64 |
| 230 | 134 | 58 |
| 154 | 112 | 73 |

Table 4. GAS CHROMATOGRAPHIC CONDITIONS

| | Column 1 | Column 2 |
|---|---|---|
| Column temperature | 150°C | Ambient |
| Injector temperature | 210°C | 180°C |
| Detector temperature | 210°C | 210°C |
| Retention time | 2.0 min | 1.3 min |

A series of low molecular weight hydrocarbons were tested as potential interferants for vinyl chloride. Retention times, relative to vinyl chloride, were determined and are listed in Table 5. The data for Column 1 was actually obtained at 100° C for Chromosorb 102 alone. At 150° C, acetaldehyde and vinyl chloride coelute on the prescribed column and are indistinguisable. Since all the samples were first analyzed on Column 1 at 150° C, the presence of a peak at the retention time of vinyl chloride may be due to acetaldehyde. Accordingly, Column 2 was used for further indentification. As indicated in Table 5, vinyl chloride and acetaldehyde are well resolved on this column.

## ADOPTED PROTOCOL

This section describes the equipment, sampling procedure, and analysis procedure used for the determination of vinyl chloride.

## EQUIPMENT

The following equipment is required for the sampling and analysis for vinyl chloride:

Charcoal, coconut, 6 to 14 mesh, Fisher Chemical

Stainless steel tubes, 3 x 1/4 in.

Air sampling pump with 1 liter/min capacity

Rotameter, 0 to 200 ml/min

3.5 ml Glass vials

Rubber-Teflon® laminated discs

Open top screw caps

Flame ionization gas chromatograph

Column: (1) 6 ft x 1/8 in. stainless steel packed with 80/100 Chromosorb 102 coupled to 6 ft x 1/8 in. stainless steel packed with 10% DC-200 on 100/120 Supelcoport; (2) 6 ft x 1/8 in. stainless steel packed with 0.4% Carbowax 1500 on Carbopak A

10 µl Syringe

Carbon disulfide

Dry ice

Table 5. RELATIVE RETENTION TIMES

| Compound | Column 1[a/] | Column 2[b/] |
|---|---|---|
| Methane | 0.15 | 0.20 |
| Ethane | 0.21 | 0.29 |
| Ethylene | 0.21 | 0.26 |
| Propane | 0.54 | 0.63 |
| Methyl chloride | 0.63 | 0.45 |
| Acetaldehyde | 0.93[c/] | 0.77 |
| Isobutane | 1.22 | - |
| Isobutylene | 1.37 | - |
| Methanol | - | 1.38 |
| 1-Butene | 1.43 | - |
| n-Butane | 1.57 | 1.83 |
| 1,3-Butadiene | 1.57 | - |
| Trans-2-butene | 1.57 | 2.92 |
| Ethyl chloride | 1.70 | 1.54 |
| Cis-2-butene | 1.73 | - |
| 1,1-Dichloroethylene | 2.00 | - |

a/ 6 ft x 1/8 in. stainless steel packed with 80/100 mesh Chromosorb 102 held at 100°C

b/ 6 ft x 1/8 in. stainless steel packed with 0.4% Carbowax 1500 on Carbopak A at ambient temperature

c/ Acetaldehyde and vinyl chloride coelute at 150°C

## SAMPLING PROCEDURE

The necessary number of charcoal tubes are prepared using the procedure outlined previously. The sealed tubes are stored in a closed glass jar until used. Air samples are collected at a rate of 100 ml/min for exactly 30 min. By the use of a calibrated rotameter, the flow rates are measured after 1, 15, and 29 min. The temperature is recorded before and after collecting the sample. Approximately 50 mg of charcoal are added to the inlet end of the tube and the tube plugged with a small portion of glass wool. Both ends of the tube are covered with aluminum foil and capped. The tube is then wrapped in aluminum foil and stored in crushed dry ice. A blank is taken to the field and treated in the same manner except that no air is drawn through it.

## ANALYSIS PROCEDURE

Vials with a 3.5 ml capacity are fitted with Teflon®-laminated septa and open-top screw caps. Exactly 2.0 ml carbon disulfide is added and the vials are placed in crushed dry ice. The glass wool plug is removed from the inlet end of the tube and the supplementary charcoal is added to the vial. The next glass wool plug is removed and the remaining charcoal is added. The vial is immediately capped, swirled to mix, and left in the dry ice for 30 min. A 5 µl portion of the carbon disulfide is injected onto the Chromosorb 102/DC-200 column held at 150° C. The next sample is injected as soon as a stable baseline is achieved. A calibration curve of peak height versus nanograms injected is prepared by analyzing standards prepared appropriately. The quantity of vinyl chloride in the carbon disulfide is calculated from observed peak height using the calibration curve. From the volume of air collected, the concentration in nanograms per liter or micrograms per liter is calculated. The results are converted to parts per billion or parts per million, respectively, by multiplying by 0.392. A recovery correction is made by multiplying the results by 1.04.

Samples believed to contain vinyl chloride are analyzed on a second column of Carbowax 1500 on Carbopak A to confirm identity.

## SECTION VI

## RESULTS AND DISCUSSION

Table 6 summarizes the results obtained for the air samples collected from the environments discussed previously. The results are presented as an observed level or as ND (not detected). The level of 10 ppb (v/v) was determined as the detection limit based upon normal protocol and was established in the following manner. It was assumed that the air sample collected was 3 liters, that 2 ml of carbon disulfide was used for desorption, and that 5 µl were injected. Setting a lower limit of absolute detection of 0.2 ng/injection, it was calculated that the air sample must be 10 ppb or greater. As reported in Table 6, no vinyl chloride was observed at or greater than 10 ppb except in the room painting environment. Samples as large as 20 to 30 liters were collected from the room which permitted lowering the detection limit to 1 ppb.

### VEHICLES

#### Automobiles, Domestic and Foreign

There was no indication of vinyl chloride in any of the automobiles sampled.

#### Mobile Homes

A peak was observed when using Column 1 for the samples collected from the new Skyline mobile home. The samples were immediately analyzed on Column 2 and no vinyl chloride peak was observed. It was concluded that no vinyl chloride was present in the mobile homes above the detection limit.

### COMMERCIAL PRODUCTS

#### Latex Paint

Latex paint may be formulated with a polymer in a water emulsion. The organic polymer in later paints sold to the general public is generally a polyvinyl acetate, polyacrylate, or a copolymer of the two.

Table 6. RESULTS OF VINYL CHLORIDE ANALYSIS

| Sample | Vinyl chloride, ppb (u/v) |
|---|---|
| Chevrolet, 1976 | ND[a] |
| 1975 | ND |
| Ford, 1976 | ND |
| 1975 | ND |
| 1974 | ND |
| Plymouth, 1976 | ND |
| 1975 | ND |
| 1974 | ND |
| AMC, 1976 | ND |
| 1975 | ND |
| 1974 | ND |
| Volkswagen, 1976 | ND |
| 1975 | ND |
| 1974 | ND |
| Toyota, 1976 | ND |
| 1975 | ND |
| Skyline, new | ND |
| used | ND |
| Champion, new | ND |
| used | ND |
| Latex paint | |
| During | 29, 15[b] |
| During and after | 4[b] |
| One day after | ND[b] |
| Vinyl wall covering | |
| Warehouse | ND |
| Showroom | ND |
| Paste | ND |
| Vinyl fabrics | |
| Pool liners | ND |
| Shower curtains | ND |
| Pull shades | ND |
| Nursery equipment | |
| New crib corner | ND |
| New crib center | ND |
| New changing table | ND |
| New toy box | ND |
| New playpen pad | ND |
| One day later - crib corner | ND |
| One day later - crib center | ND |
| One day later - changing table | ND |
| One day later - toy box | ND |

a/ Unless otherwise noted, ND = not detected above 10 ppb (v/v).
b/ Detection limit of 1 ppb (v/v).

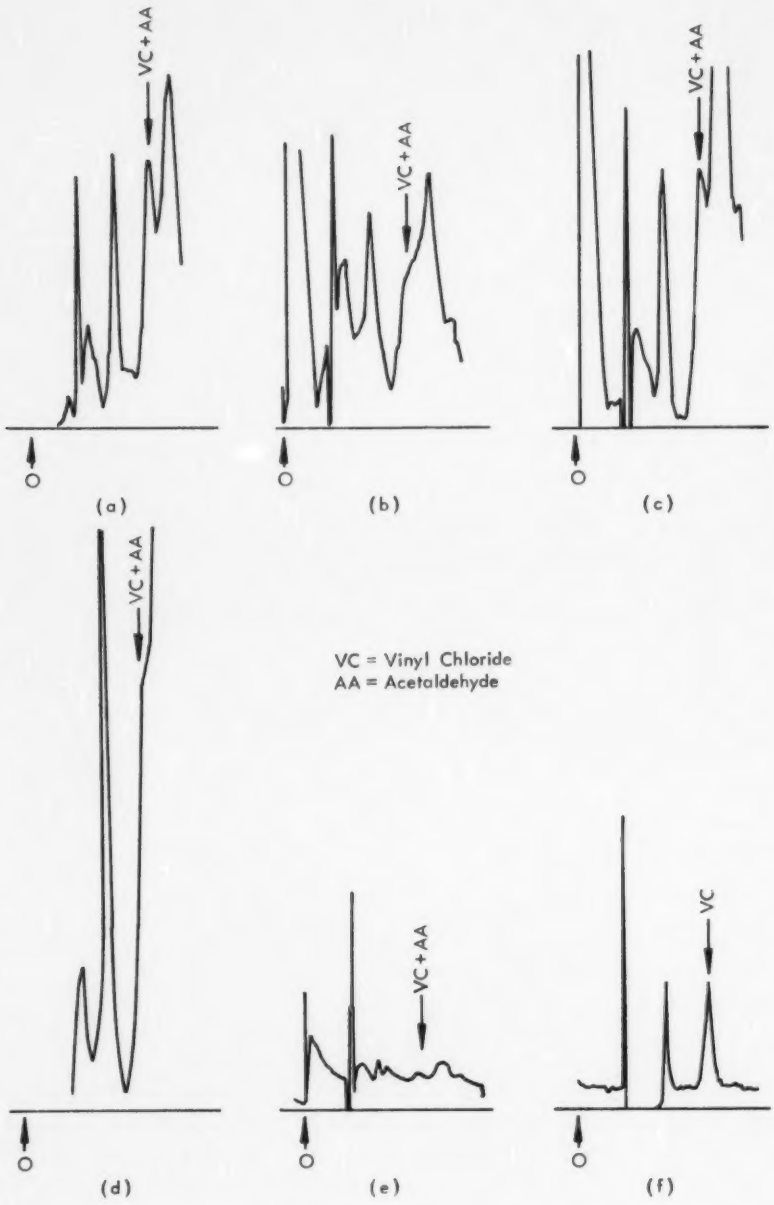
Six major paint manufacturers in the Midwest were contacted in an attempt to determine if polyvinyl chloride is used in paint formulation. The following companies responded that they did not use polyvinyl chloride: Benjamin Moore, Pratt and Lambert, Colony Paint, Great Western, and Davis. Cook Paint Company, 1412 Knox, Kansas City, Missouri, reported a limited use of polyvinyl chloride in latex paint. A terpolymer of vinyl chloride, vinyl acetate and ethylene is used in what is termed by Cook Paint Company as accent colors. These paints are deeply colored and highly pigmented. According to the company, this line of paints represents a minor fraction of all latex paints. The terpolymer used by Cook Paint Company is produced as Airflex 728 by Air Products and Chemicals.

Duplicate 30 min air samples were collected starting at 2-1/2 hr after the painting began. The samples were first analyzed using Column 1. A peak was observed at the retention time of vinyl chloride as shown in Figure 2. The samples were then analyzed on Column 2 to establish whether vinyl chloride or acetaldehyde was being detected. As seen in the chromatograms illustrated in Figure 3, peaks were observed both at the retention time of vinyl chloride and acetaldehyde, thus confirming their presence. A single 4-hr sample collected later the same day also showed the presence of vinyl chloride and acetaldehyde. This sample was collected during the last 2 hr of painting and for 2 hr after the painting was completed. A final set of 4 hr duplicate samples were collected from 0900 to 1300 the following day and did not contain vinyl chloride. The level of vinyl chloride for the three sampling periods was 22 ppb, 4 ppb, and not detected, respectively. The room had normal forced air ventilation, and the decrease in vinyl chloride was as expected.

Vinyl Wall Covering

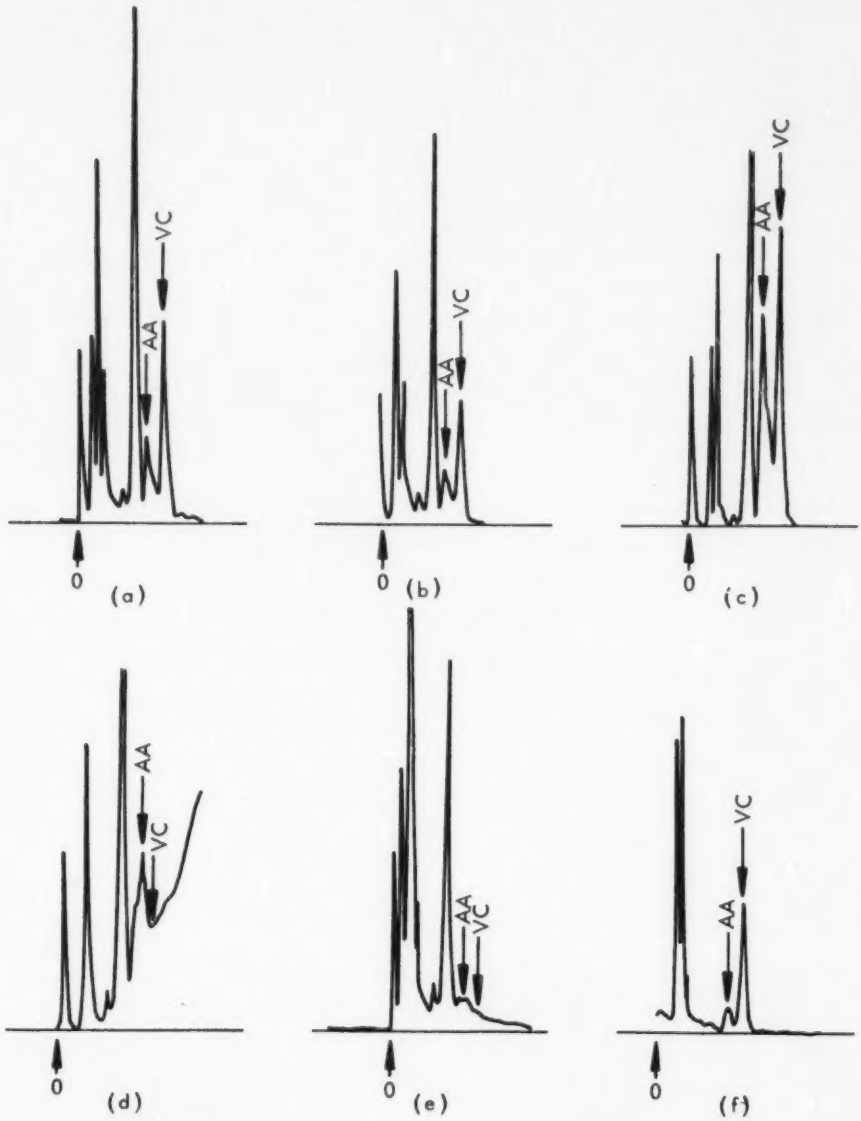
The air samples collected from the warehouse region, after analysis on both columns, did not contain detectable levels of vinyl chloride. The presence of acetaldehyde, however, was strongly indicated. The air samples collected from the showroom contained neither vinyl chloride nor acetaldehyde. Since no vinyl chloride was found in these environments, it was decided to not sample a room being wall papered.

A sample of commercial ready-to-use vinyl wallpaper adhesive, purchased from Montgomery Wards and Company, Inc., was tested for vinyl chloride. A 6.0 g sample was placed in a 7.5 ml septum-equipped vial and heated to 60°C for 30 min. The head space was sampled by a gas-tight syringe and did not contain vinyl chloride.




(a) Sample collected during painting
(b) Duplicate
(c) Sample collected during and after painting
(d) Sample collected 24 hr later
(e) Blank
(f) Standard, 0.45 ng

Figure 2. Chromatograms from latex-painted room - Column 1




VC = Vinyl Chloride
AA = Acetaldehyde

(a) Sample collected during painting
(b) Duplicate
(c) Sample collected during and after painting
(d) Sample collected 24 hr later
(e) Blank
(f) Standard, 0.25 ng

Figure 3. Chromatograms from latex-painted room - Column 2

Vinyl Fabrics

The air samples collected in the vicinity of the vinyl swimming pool lines did not contain detectable levles of vinyl chloride. Vinyl shower curtains and vinyl pull shades were two other fabrics which were checked as sources of vinyl chloride. The air samples removed from the closed chambers did not show the presence of vinyl chloride although acetaldehyde was indicated. Temperature had no effect. Due to the negative findings, no rooms containing these products were sampled.

Nursery Equipment

No vinyl chloride was detected in the analysis of air samples collected from nursery environments.

Vinyl Repair and Welding

Sheets and films of polyvinyl chloride can be repaired or welded together by the application of heat. Welding is done typically with a stream of air heated to 260 to 290° C.

At these temperatures, it is reasonable to expect that any entrapped vinyl chloride would be released. A study has been made by the Environmental Health Laboratory,[2/] McClellan Air Force Base, California, which reported that no vinyl chloride was detected at the 0.1 ppm level during welding and meat-wrapping operations.

REFERENCES

1. "Preliminary Assessment of the Environmental Problems Associated with Vinyl Chloride and Polyvinyl Chloride," EPA-560/4-75-001, September 1974.

2. Smith, B. S., et al., "Evaluation of Vinyl Chloride Associated with Heat Sealing PVC Products," Environmental Health Laboratory, McClellan Air Force Base, California, Prof. Report No. 74M-17, December 1974.